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PREPARATION OF TOOTHPASTE  
[Renshma no seizohoho]

Masahiro Takizawa, et al.

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INVENTOR (72) : TAKIZAWA, MASAHIRO; OKINO, TORU

APPLICANT (71) : LION CORP.

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## 1. Name of this Invention

Preparation of Toothpaste

## 2. Claim(s)

[Claim 1] Preparation of toothpaste comprising a step of mixing a polishing agent with water or a mixed solution of water with a wetting agent, a step of deaerating the resultant mixture with stirring under reduced pressure, and a step of adding a binder dispersed in the wetting agent thereto.

[Claim 2] Preparation of toothpaste according to Claim 1, wherein one part wt. polishing agent is incorporated with at least 0.5 pts. wt. of water or a mixture solution of the water and a wetting agent.

[Claim 3] Preparation of toothpaste according to Claim 1 or 2, wherein said polishing agent is mixed in water or a mixture solution of water and a wetting agent and deaerated with stirring under reduced pressure of 10 - 200 mmHg measured as absolute pressure.

[Claim 4] Preparation of toothpaste according to Claim 1 or 2, wherein said polishing agent is mixed in water or a mixture solution of the water and a wetting agent under normal pressure and then deaerated with stirring under reduced pressure of 10 - 200 mmHG.

[Claim 5] Preparation of toothpaste according to Claims 1 - 4, wherein said polishing agent is mixed in water or a mixture solution

\* Numbers in the margin indicate pagination in the foreign text.

of the water and a wetting agent to prepare a slurry, and this slurry is mixed with a fragrance and surfactant.

[Claim 6] Preparation of toothpaste according to Claim 5, wherein said fragrance and surfactant are added to said slurry under reduced pressure of 10 - 200 mmHG absolute pressure.

[Claim 7] Preparation of toothpaste according to Claims 1 - 6, wherein 1 wt. part binder is dispersed in 2 - 10 wt. parts wetting agent.

[Claim 8] Preparation of toothpaste according to Claims 1 - 7, wherein said binder dispersed in a wetting agent is added under reduced pressure for making the binder swollen and dissolved.

### 3. Detailed Explanation of this Invention

#### [Technological Field]

This invention pertains to an efficient manufacturing method of stable toothpaste not containing air bubbles.

#### [Description of the Prior Art]

To prepare a toothpaste, a mixture of refined water and a polishing agent, such as calcium secondary phosphate dehydrate, a surfactant such as high class alkyl sulfate, a wetting agent such as glycerin, and a binder such as carboxy methyl cellulose, and also a sweetener, fragrance, a medicinal substance, etc., are combined and blended uniformly, thereby creating a paste having fluidity or a gel with low fluidity. In this case, the manufacturing method of

toothpaste is preferably efficient and highly productive.

Furthermore, if air bubbles (air) is mixed in the toothpaste, not only the appearance worsens, but also the quality of the toothpaste lowers. Therefore, the air bubbles (air) must be removed from the toothpaste as much as possible. Particularly, for a transparent toothpaste, mixed air bubbles lowers the transparency of the toothpaste and may make the toothpaste semi-clear or non-transparent. Therefore, removal of air bubbles must be through and strict during the production process.

Conventionally, as the industrial production method of toothpaste, a binder is made to swell and be dissolved in a wetting agent, refined water, etc., while the mixture is heated if necessary so as to prepare a viscous swollen solution. Next, powder of a polishing agent is kneaded into this swollen solution, to which a surfactant, fragrance, medicinal substance, etc. are added and blended to form a uniform mixture. Then, air is removed from the mixture for preparing a toothpaste. However, based on this method, after said swollen solution is typically a viscous high molecular solution having a high viscosity value of 100 - 400 poise (value obtained by measuring at 20 rpm for 2 - 3 min. using a BH type rotary viscosity measurement device), a polishing agent is added for an amount which is 0.6 - 1.2 times of the solution weight and kneaded with the viscous solution. As a result, coagulated blocks are formed by the mutual reaction of the polishing agent powder and swollen

solution during the kneading process, thereby subsequently creating a super viscous mixture. Thus, a significant amount of energy and long time of kneading are necessary for homogenizing the viscous mixture. Moreover, as described above, when air is mixed in the toothpaste, the substances in the toothpaste are oxidized to change the quality and color of the toothpaste. Therefore, air in the toothpaste must be eliminated as much as possible. In the abovementioned production process, this air removing process is performed parallel to the process of homogenizing the mixture or after the homogenizing process. However, in either case, a long time of deaeration process is needed for removing the air bubbles from the highly viscous toothpaste. Moreover, since it is impossible to remove fine air bubbles thoroughly, about 2 - 5 volume % of air bubbles remain in the toothpaste. In this case, even if the air bubbles mixed in the toothpaste is only a small amount (2 - 5 volume %) which is the amount unrecognizable visually, when the toothpaste is stored for a long period lasting about several months - 3 years, the quality and color of the toothpaste may change due to oxidization with the air existing in the fairly small amount of air bubbles. Particularly, this oxidizing problem tends to affect the medicinal ingredients more significantly by lowering their effectiveness. Therefore, with the industrial production of toothpaste, after polishing agent powder is kneaded into a viscous high molecular swollen solution, coagulated blocks formed during the kneading process are broken into pieces for

homogenizing the mixture. Moreover, as an air-removing process (deaeration) is performed to a highly viscous material, the productivity is extremely low. Hence, a method which can improve the productivity and is capable of thorough deaeration is needed by the industry.

To solve the abovementioned problems, JP S52-108031 reported a toothpaste production method which adds a powder mixture consisting of a polishing agent, binder, and foaming agent and also fragrance in water simultaneously within a short time, blends these powders, fragrance, and water by stirring at 600 rpm of rotations so as to prepare a raw paste material, and deaerates this raw paste under reduced pressure. This method is a preferable technique, as it can reduce the production time of toothpaste compared with the conventional method, thereby being able to improve the productivity. However, in order to prevent the deterioration of binder during mechanical shearing under high speed stirring exceeding 600 rpm, the stirrer conditions, such as rotation count, stirring time, etc., must be set up strictly corresponding to the raw materials, particularly associated with the binder lot. In addition, the method has a problem of deaerating a highly viscous raw paste containing a swollen and melted binder. Moreover, the toothpaste production method disclosed in JP S35-7699 has the same problem of deaerating a highly viscous raw paste containing a swollen and melted binder, under reduced pressure.

Furthermore, based on the method disclosed in JP S48-40947, a mixture from which the gases in the liquid medium, gelling agent, and polishing agent are removed, or a mixture not containing any gas is prepared. Then, a mixture consisting of a synthetic organic cleaning agent fundamentally not containing any gas and a liquid medium is produced. Thus, a paste or gel form of toothpaste not containing gas can be prepared by homogenizing these mixtures. The drawbacks of this method are that it is difficult to improve the productivity of this method, since it requires (1) an inefficient kneading process which kneads polishing powder into a highly viscous solution containing a swollen and dissolved binder powder and then homogenizes the mixture, (2) deaeration process which heats the mixture or leaves the mixture unattended for a long time in order to remove air bubbles in the synthetic organic cleaning agent and polyvalent alcohol mixed aqueous solution, and moreover, (3) inefficient mixing process which blends a synthetic organic cleaning agent into an extremely viscous mixture prepared by kneading the polishing powder to a paste containing a swollen and dissolved binder. Moreover, this method is not easily used with a system not containing much polyvalent alcohol.

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The developers of this invention thoroughly investigated a method which could prevent air bubbles from mixing into the toothpaste in order to mass-produce high quality toothpaste consisting of a smooth base and not causing denaturing during storing

time. As a result, they discovered that, by utilizing the toothpaste production method comprising a step of mixing 1 wt. part of a polishing agent with at least 0.5 wt. parts of water or a mixed solution of the water with a wetting agent, a step of deaerating the resultant mixture, and a step of adding a binder dispersed in the wetting agent thereto to make the binder swollen and dissolved, the homogenization of the substances at low viscosity and removal of air bubbles became possible. Thereby, efficient mass production of high quality toothpaste not containing air bubbles can be assured, which subsequently lead to accomplishing the object of this invention.

The following explains this invention in detail.

The toothpaste production method based on this invention characteristically mixes 1 wt. part of a polishing agent with at least 0.5 wt. parts of water or a mixed solution of the water with a wetting agent, deaerates the resultant mixture, and adds a binder dispersed in the wetting agent thereto to make the binder swollen and dissolved. Thereby, this invention can produce a toothpaste which has smooth base texture, excellent appearance, and characteristic highly favorable to users, and moreover, hardly causes denaturing when stored for a long time, being able to maintain the effect of medicinal contents.

Examples of a polishing agent are calcium secondary phosphate, calcium secondary phosphate in the form of dihydrate or anhydride, calcium third phosphate dehydrate, calcium carbonate, aluminum

hydroxide, aluminum, insoluble meta phosphoric acid sodium, pyrrolic acid calcium, crystallizing silica, non-crystallizing silica, magnesium carbonate, magnesium phosphoric acid, synthetic resin powder, etc., where one or more kinds of these materials can be used. The particle diameter of these polishing agent is not particularly limited, as it can be any appropriate value corresponding to the required polishing effect. However, the average diameter is normally 1 - 20 µm. The hardness is preferably not excessive so that the tooth enamel is not damaged, where a material with a Morse hardness of 3 or below is used. Moreover, although the amount of polishing agent is not particularly limited, it is normally 20 - 60% (wt. %; hereafter, % denotes wt. %) of the entire toothpaste amount.

Moreover, examples of a wetting agent are polyvalent alcohol, such as glycerin, propylene glycol, sorbitol, polyethylene glycol, polypropylene glycol, xylitol, maltitol, lactitol, etc. One or more of these materials may be used. Although the using amount depends on the kind of toothpaste, it is usually 5 - 70% of the overall tooth paste. Moreover, when glycerin and/or propylene glycol and sorbitol (normally used in the form of aqueous solution) are combined, the ratio of glycerin and/or propylene glycol and sorbitol aqueous solution (50 - 80% solution) is 1 : 20 - 10 : 1 (in weight), particularly preferably 1 : 15 - 1 : 1.

Furthermore, binders are materials which can be swollen and solved in water. Examples are cellulose derivatives, such as carboxy

methyl cellulose sodium, methyl cellulose, hydroxyl ethyl cellulose, etc., alkali metal alginate, such as carrageenan, alginic acid sodium, etc., gum materials, such as quithanthene gum, tragacant gum, karaya gum, Arabic gum, etc., synthetic binders, such as polyvinyl alcohol, polyacrylic acid sodium, carboxy vinyl polymer, etc. One or more kinds of these materials may be used. In this case, the particle diameter of the binder is determined based on the kind of binder material. Moreover, although the amount of binder is not particularly limited, the regularly used amount is 0.3 - 5% of the total toothpaste.

Based on this invention, preferably at least 0.5 wt. parts, more preferably at least 0.7 wt. parts of water or a mixture solution consisting of water and a wetting agent is blended in 1 wt. part of polishing agent described above, and then, the mixture is deaerated.

To perform this operation, for example, water is first put in a tank equipped with a stirrer capable of stirring the whole fluidal body, and after a wetting agent is added if necessary, the materials are blended. In the phase, the viscosity of the mixture is usually 1 poise or less. Next, after a polishing agent is added, the mixture is dispersed and blended. For this process, the mixture can be deaerated under reduced pressure by reducing the inner pressure of the tank from the phase of dispersion-mixing the polishing agent. However, since the viscosity of the slurry is normally 20 poise or less when 1 wt. part of polishing agent is dispersed and mixed in 0.5

wt. part of water or a mixed solution consisting of water and a wetting agent for preparing the slurry, stirring the mixture under normal pressure can remove the air bubbles almost completely. In this case, if the amount of water or a mixed solution blended with 1 wt. part of polishing agent is less than 0.5 wt. parts, air bubble may not be removed thoroughly. Therefore, as described above, water or a mixed solution of water and a wetting agent is preferably 0.5 wt. parts or more.

When the abovementioned dispersing and blending the polishing agent is performed under normal pressure, the inner pressure of the tank after this process is preferably arranged to reduced pressure, as this arrangement can remove the air bubbles completely. In this case, the vacuuming ratio is preferably 10 - 200 mmHg (measured as absolute pressure).

As described above, the method based on this invention first disperses and mixes a polishing agent in water or a mixed solution of the water with a wetting agent, and deaerates the mixture to remove the air bubbles brought into the system by the polishing agent. In this case, in addition to the abovementioned substances, other substances, such as surfactant, sweetener, fragrance, antiseptic, medicinal substance, etc. may be added during or after the abovementioned operation if necessary.

Examples of a surfactant are anionic activators, such as lauryl sodium sulfate, myristyl sodium sulfate, palmityl sodium sulfate,

high class fatty acid soap,  $\alpha$ -olefin sulfonic acid sodium, etc., nonionic activator, such as lauryl diethanol amide, sugar fatty acid ester, polyoxy ethylene sorbitan monolaurate, etc., and amphoteric activators. One or more kinds of these materials are usually used for an amount of 0.1 - 7% of the whole toothpaste. Although these surfactants in a form of powder may be mixed with a polishing agent, and the mixture may be added to water or a mixed solution of the water and a wetting agent, the preferable method is that the surfactants are added into a slurry prepared by dispersing a polishing agent in water or a mixed solution consisting of the water and a wetting agent. In this case, although the surfactants may be directly added to the slurry containing a dispersed polishing agent, the surfactants are preferably added in water or a mixed solution of the water and a wetting agent beforehand. Moreover, when a mixed solution consisting of water and a wetting agent is used, the mixing ratio of wetting agent is preferably at least 4 wt. parts to 1 wt. part of water.

As the sweetening agent, sodium saccharide, sucrose, maltose, lactose, perillartin, stevioside, glytyl lysine salt, etc. may be used for an amount of 0.05 - 5% normally. These materials may be dissolved in water or a mixed solution of the water and a wetting agent prior to dispersing a polishing agent, or after the powder form of sweetener is mixed with a polishing agent, the prepared mixture can be added to water or a mixed solution of the

water with a wetting agent. Moreover, the sweetener may be dissolved in the slurry in which a polishing agent is dispersed. Furthermore, as the fragrance, refined oil, such as spearmint oil, peppermint oil, salvia oil, eucalyptus oil, lemon oil, lime oil, winter green oil, cinnamon oil, etc., other spices and fruit flavors, separated or synthesized fragrance of *l*-menthol, carbon, anethol, eugenol, etc., may be added for an amount of 0.1 - 5%. Although they can be dispersed in a polishing agent, etc. beforehand, these fragrances are preferably mixed in a slurry prepared by dispersing a polishing agent.

As an antiseptic agent, paraoxy benzoic acid ethyl, paraoxy benzoic acid butyl, etc. may be used. Examples of medicinal components are enzymes, such as dextranase, lytic enzyme, lysozyme, amylase, bacteria-dissolved enzyme, etc., anti-plasmin agent, such as epsilon amino capron acid, Tranechisom (transliterated) acid, etc., fluorine compounds, such as sodium fluoride, monofluoro phosphoric acid sodium, first tin fluoride, chloro hexidin salt, fourth class ammonium salt, aluminum chloro hydroxyl arantoin, glycyl lysine acid, chrolophyl, sodium chloride, phosphoric acid compound, etc. Moreover, silica gel, aluminum silica gel, organic acid, and salts of organic acid, etc. may be composed if needed. To add these components, depending on their formations, solubility in water, etc., if it is in a powder form insoluble in water, for example, the material is mixed with a polishing agent; if it is soluble in water,

the material is added to water or a mixed solution of the water with a wetting agent or to a slurry prior to dispersing a polishing agent. Moreover, if it is oil-like or soluble in oil, it may be mixed with fragrance or added directly to a slurry to which a polishing agent is dispersed.

Based on this invention, for adding a surfactant, fragrance, etc., to the slurry containing a dispersed polishing agent, the process is preferably performed under reduced pressure, particularly preferably 10 - 100 mmHg (absolute pressure). The viscosity even during the phase of mixing a surfactant is normally 25 poise or less. Moreover, as the process is performed under reduced pressure, the air bubbles brought by the surfactant, etc. can be removed assuredly, thereby not leaving any possibility of air bubble existence. The Sequence for adding the surfactant, fragrance, etc. is not restricted. /47

Based on this invention, after the abovementioned process is performed, a binder is added as the last material and made swollen and dissolved to obtain the toothpaste. In this case, the binder is dispersed in a wetting agent beforehand. By adding the binder which is dispersed in a wetting agent, a toothpaste with excellent smoothness can be obtained. However, if the binder is directly added, as the swelling of binder swelling tends to become uneven, satisfactory toothpaste cannot be obtained. Moreover, when dispersing a binder in a wetting agent, the ratio is preferably at

least 2 wt. parts of wetting agent to 1 wt. part of binder. In addition, the processes of adding, swelling, and dissolving this binder may be performed under normal pressure or reduced pressure, where the reduced pressure is preferred.

Although the abovementioned operations (process of dispersing the polishing agent; process of making the binder swollen and dissolved, etc.) may be performed under heating, each operation may be performed at room temperature.

With the abovementioned production method of toothpaste, a polishing agent and surfactant used if needed are added to water or a mixed solution of the water with a wetting agent. Since a powder component having a large amount of air bubbles can be dispersed and mixed at low viscosity (normally 30 poise or less), removal of air bubbles can be easily and speedily performed. Particularly, by removing air bubbles under reduced pressure, complete air bubble removal can be assured. Moreover, since mixing of air bubbles can be prevented to the last process which makes the binder swell and dissolved, the obtained toothpaste does not contain air bubbles. Therefore, the method based on this invention can be effectively applied for producing transparent toothpaste. In addition, as the toothpaste produced by the method based on this invention does not contain air bubbles, denaturing of the ingredients of the toothpaste caused by air bubbles can be prevented during a long period of storing. Furthermore, as described above, since the air bubbles can

be removed easily and speedily, the production of toothpaste does not necessarily require stirring under heating or strong shearing for removing the air bubbles. Therefore, the appearance and stability of the product can be improved. In addition, air bubbles are released quickly, and foaming or swelling of slurry while air bubbles are removed can be prevented effectively. Hence, a small volume mixer device can be used for producing toothpaste. As a result, the equipment size can be minimized.

Furthermore, based on the production method of this invention, a binder dispersed in a wetting agent is added lastly, allowing the binder to swell and be dissolved. Also, since the surfactant is added prior to adding a binder, the surfactant can improve the hydrophilic property of the polishing agent to prevent the binder from coagulating during swelling. Thus, the obtained toothpaste is smooth and has excellent shininess and density, thereby providing excellent appearance.

The following describes the operational examples of this invention for explaining this invention in concrete manner.

Operational example 1:

Secondary phosphoric acid calcium	40%
Sorbitol (60% aqueous solution)	30
Glycerin	5
Lauryl sodium sulfate	2
Carboxy methyl cellulose sodium	1.5
Sodium saccharide	0.2
Fragrance	1.0
Paraoxy benzoic acid ethyl	0.001
Water	<u>Remaining amount</u>
	100.0%

Water was put in a vacuuming type stirrer tank equipped with a stirrer capable of stirring the whole content, to which sodium saccharide and paraoxy benzoic acid ethyl were added and mixed/dissolved. During this process, the mixture was stirred at 25°C for 10 min. Moreover, a sorbitol aqueous solution was added and mixed. The viscosity was 1 poise or less in this phase.

Next, second phosphoric acid calcium was added to this aqueous solution and stirred for 5 min. The viscosity in this phase was 30 poise or less. Moreover, during stirring, air bubbles in the powder substances (second phosphoric acid calcium) were almost completely removed.

Next, after the inside of the stirring tank was vacuumed to the pressure of 700 mmHg (absolute voltage = 60 mmHg) using a vacuuming pump, and fragrance was added, the mixture was stirred for 3 min. Then, lauryl sodium sulfate was added to the mixture and stirred for 5 min. As the viscosity at this time was 10 poise or less, defoaming and mixing can be effectively and easily performed.

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Lastly, carboxy methyl cellulose sodium wetted in glycerin under vacuumed atmosphere at 60 mmHg (absolute pressure) was added under stirring so as to make it swell and be dissolved. Thus, a toothpaste was formed.

The obtained toothpaste did not contain air bubbles, and provided excellent density and shininess with smoothness and stability.

With the abovementioned method, since a polishing agent and surfactant were mixed at low viscosity, air bubbles in the powder could be released quickly while the slurry is not foamed or swollen by the mixed air bubbles. Therefore, unlike the conventional device, the device volume does not need to be increased to twice the actual toothpaste volume, where 1.2 times of the actual toothpaste volume was sufficient as the device size based on this invention. Moreover, since this invention did not require any special operation, such as stirring the mixture at a high temperature for removing air bubbles, the production time could be shortened, and the operation was convenient for providing stability to the toothpaste quality.

Operational example 2:

Glycerin	27
Calcium silicate	2.0
Carboxy methyl cellulose sodium	0.6
Sodium saccharide	0.2
Sorbitol (70% aqueous solution)	40
Die solution (1% water base)	0.2
Fragrance	1.2
Lauryl sodium sulfate	2.0
Peroxy benzoic acid ethyl	0.001
Water	<u>Remaining amount</u>
	100.0%

Peroxy benzoic acid ethyl and sodium saccharide were added in purified water in a stirring tank for high viscosity substances, to which a sorbitol aqueous solution, glycerin, and die solution were added and mixed. Then, calcium silicate was added to the solution and stirred for 5 min. Next, after the inside of the stirring tank was vacuumed (absolute pressure = 30 - 100 mmHg), fragrance, and lauryl sodium sulfate which was mixed in a glycerin aqueous solution (80%) at the weight ratio of 1 : 4 beforehand were added and mixed.

Lastly, while the vacuumed state was maintained, carboxy methyl cellulose sodium, which was dispersed in 100% glycerin at the weight ratio of 1 : 5 beforehand, was mixed so that it could be swollen and dissolved. Subsequently, toothpaste could be produced.

The obtained toothpaste was free from air bubbles and visually transparent with excellent smoothness, shininess, and stability.

With this type of transparent toothpaste, existence of air bubbles is not preferable for its appearance. However, the

conventional production method, which deaerates the material at high viscosity (300 poise or higher) after the binder is swollen and wetted, cannot provide complete deaeration. On the other hand, since the method based on this invention disperses calcium silicate or lauryl sulfate sodium having abundant air bubbles in water or polyvalent alcohol of low viscosity, air bubbles can be removed easily and assuredly, and moreover, thorough air bubble removal can be accomplished within a short time.